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A review of working fluid and expander selections for organic Rankine cycle

Junjiang Bao, Li Zhao *

Key Laboratory of Efficient Utilization of Low and Medium Grade Energy, MOE, Tianjin University, No. 92 Weijin Road, Tianjin 300072, People' Republic of China

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A B S T R A C T

How to effectively utilize low and medium temperature energy is one of the solutions to alleviate the energy shortage and environmental pollution problems. In the past twenty years, because of its feasibility and reliability, organic Rankine cycle has received widespread attentions and researches. In this paper, it reviews the selections of working fluids and expanders for organic Rankine cycle, including an analysis of the influence of working fluids' category and their thermodynamic and physical properties on the organic Rankine cycle's performance, a summary of pure and mixed working fluids' screening researches for organic Rankine cycle, a comparison of pure and mixture working fluids' applications and a discussion of all types of expansion machines' operating characteristics, which would be beneficial to select the optimal working fluid and suitable expansion machine for an effective organic Rankine cycle system.

Contents

* Corresponding author. Tel.: +86 22 27890051; fax: +86 22 27404188.
E-mail address: jons@tju.edu.cn (L. Zhao).

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1. Introduction

The invention of the electric power is the core impetus of the second industrial revolution, and steam Rankine cycle driven by fossil fuels is still the dominant power supply method. As is known to all, the accelerated consumption of fossil fuels has caused many serious environmental problems such as air pollution, global warming, ozone layer depletion and acid rain [1]. How to effectively utilize low and medium temperature energy which is vast but undeveloped is one of the solutions to alleviate the energy shortage and environmental pollution problems. However, many problems are encountered when using water as working fluid for steam Rankine cycle [2]:

- need of superheating to prevent condensation during expansion
- risk of erosion of turbine blades
- excess pressure in the evaporator
- complex and expensive turbines

Various thermodynamic cycles such as the organic Rankine cycle, supercritical Rankine cycle, Kalina cycle and trilateral flash cycle have been proposed and studied for the conversion of low-grade heat sources into electricity [3]. Compared with the Kalina cycle's complex system structure, trilateral flash cycle's difficult two-phase expansion and supercritical Rankine cycle's high operating pressure, organic Rankine cycle has the characteristics of simple structure, high reliability and easy maintenance. Organic Rankine cycle, which has the same system configuration as steam Rankine cycle but uses organic substances with low boiling points as working fluids, can use various types of heat source, including industrial waste heat [4,5], solar energy [6,7], geothermal energy [8,9], biomass energy [10,11] and ocean energy [12] etc. Meanwhile, in order to improve energy utilization, it can be easily combined with other thermodynamic cycles, such as the thermoelectric generator [13,14], fuel cell [15], internal combustion engine [16–19], micro turbine [20], seawater desalination system [21–23], Brayton cycle [24,25] and gas turbine-modular helium reactor (GT–MHR) [26,27]. Furthermore, it also can be used as prime movers of combined cooling and power system [28,29], CHP [10,30,31] and CCHP [32,33] systems.

Chen et al. [3] summarized pure working fluids which were suitable to subcritical and supercritical organic Rankine cycle, but mixed working fluids were not included, and furthermore, the comprehensive pure working fluid candidates and the optimal ones are not reviewed; Tchanche et al. [2] and Fredy et al. [81] made comprehensive reviews of organic Rankine cycle for all kinds of applications; Qiu et al. [82] reviewed various expansion machines, but the main purpose of their study was to select a expander applied in micro CHP systems and the large numbers of experiments and comparisons among different types of expanders are also not covered. Because the rapid development in the researches of organic Rankine cycle's working fluid and expansion machine and their selections play a key role in organic Rankine cycle performance and economy, this paper has done a comprehensive review about them. As to working fluids, first of all, the influences of the working fluids' types and thermal physical properties on organic Rankine cycle performance are discussed; secondly, the researches of pure and mixed working fluids are summarized, including the discussion of the working fluids' screening results, the comparison of the pure and mixed working fluids and the clarification of mixture ORC advantages and disadvantages; finally, some limitations in the process of the working fluids' screening are discussed. Regarding to the expansion machines, first all types of expansion machines' operating characteristics are analyzed; second various types of expansion machine prototypes' researches are summarized; finally, the applicable scopes of different types of expansion machine are compared, which is beneficial to ORC expansion machine selection during the design process.

2. Working fluid selection

Because affecting the efficiency of system, the sizes of the system components, the design of expansion machine, the system stability and safety and environmental concerns, the selection of working fluids is very important for the ORC system performance

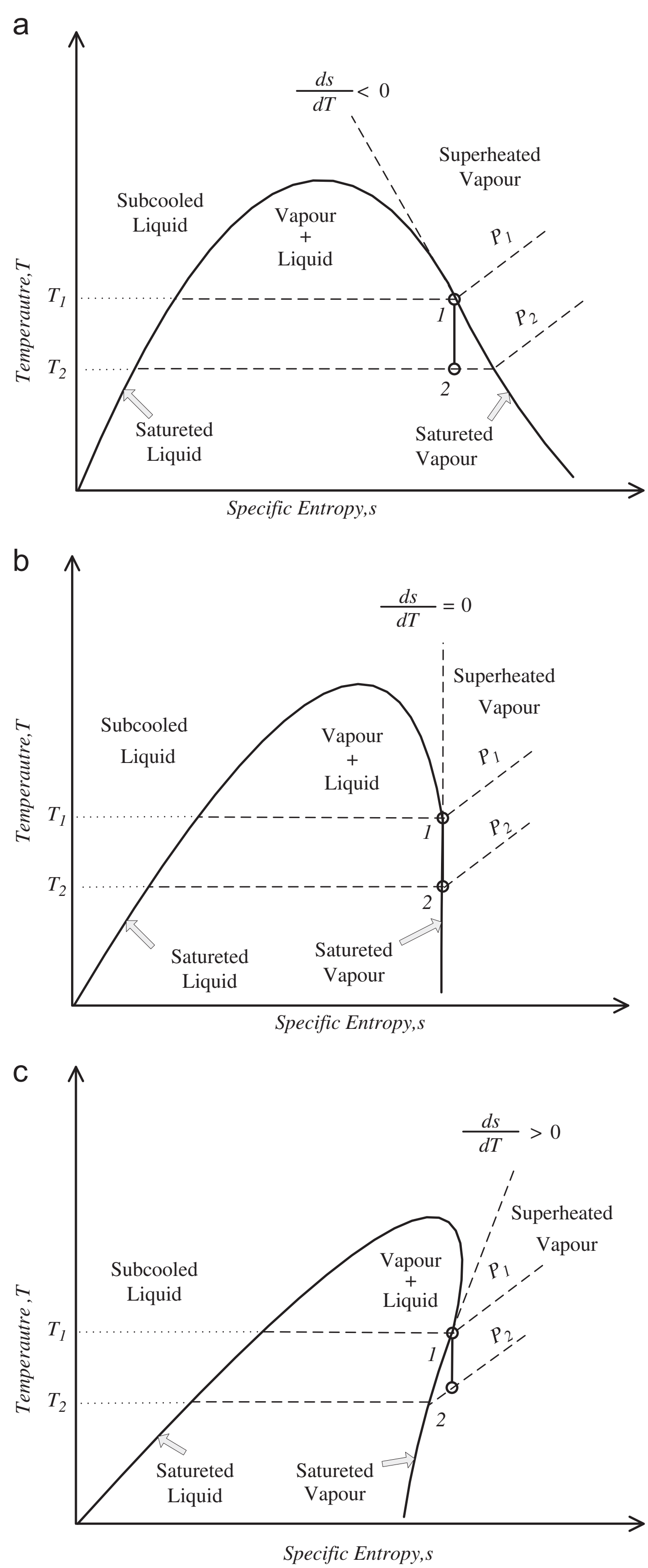

Fig. 1. Diagram T–s for fluids (a) wet, (b) isentropic and (c) dry [38].

and economy [34–36]. Different from the characteristics of other thermodynamic cycles, such as compression refrigeration cycle (working conditions are determined) and Kalina cycle (working fluid composition is set although mass fractions vary), working fluid selection of ORC system is a more complicated task owing to the following two reasons basically:

1. The working conditions and heat source types of ORC vary widely: from low-temperature heat source of 80 °C (e.g. geothermal, plate type solar collector) to high- temperature of 500 °C heat source (e.g. biomass).
2. Except for some substances whose critical temperatures are too low or too high, hundreds of substances can be used as working fluid candidates of ORC, including hydrocarbons, aromatic hydrocarbons, ethers, perfluorocarbons, CFCs, alcohols, siloxanes and inorganics (which should not inherently not be an ORC but due to the similarity with ORC so that included) etc.

2.1. Working fluids' category and their thermodynamic and physical properties

2.1.1. Working fluids' category

Except for the structural point of view and type of atoms in the fluid molecule, the working fluids could be categorized according to the saturation vapor curve, which is one of the most crucial characteristics of the working fluids in an ORC [4]. This characteristic affects the fluid applicability, cycle efficiency, and arrangement of associated equipment in a power generation system [37]. As shown in Fig. 1 [38], there are generally three types of vapor saturation curves in the temperature-entropy (*T*–*s*) diagram: a dry fluid with positive slopes, a wet fluid with negative slopes, and an isentropic fluid with nearly infinitely large slopes. The examples of wet fluids are water and ammonia. It is observed from the *T*–*s* diagram that a superheater is employed to superheat the vapor. The saturated vapor phase of a dry fluid becomes superheated after isentropic expansion. An isentropic fluid has a nearly vertical vapor saturation curve, e.g. R11 and fluorinal 85. Since the vapor expands along a vertical line on the *T*–*s* diagram, vapor saturated at the turbine inlet will remain saturated throughout the turbine exhaust without condensation. The features of persistent saturation throughout expansion and the fact that there is no need for installing a regenerator makes isentropic fluids become ideal working fluids for ORCs [4,37].

Due to the negative slope of the saturation vapor curve for a wet fluid, outlet stream of the turbine typically contains lot of saturated liquid. Presence of liquid inside turbine may damage turbine blades and it also reduces the isentropic efficiency of the turbine. Typically, the minimum dryness fraction at the outlet of a turbine is kept above 85%. To satisfy the minimum dryness fraction at the outlet of the turbine, wet fluid at the inlet of the turbine should be superheated [39]. Due to reduction in heat transfer coefficient in the vapor phase, heat transfer area requirement and hence, the cost of the superheater goes up significantly. There are other operational issues related to the superheater as well. While "isentropic" and "dry" fluids do not need superheating, thereby eliminating the concerns of impingement of liquid droplets on the expander blades. Moreover, the superheated apparatus is not needed. Therefore, the working fluids of "dry" or "isentropic" type are more adequate for ORC systems [39,40]. If the fluid is "too dry," the expanded vapor will leave the turbine with substantial "superheat", which is a waste and adds to the cooling load in the condenser [3]. Usually a regenerator is used to reclaim these exhaust vapor to increase the cycle efficiency; however, it would increase the system's initial investment and complexity, which exists trade-off. Therefore, Hung et al. [4] thought that isentropic fluids are most suitable for recovering low-temperature waste heat. In their latter research [41] about the influence of types of the saturation vapor curve for a fluid on system efficiency and irreversibility, results indicated that wet fluids with very steep saturated vapor curves in *T*–*s* diagram have a better overall performance in energy conversion efficiencies than dry fluids and isentropic fluids. They are not always suitable for ORC systems when other thermo physical properties are taken into consideration.

With respect to the overheating, Hung et al. [4] found for operation between two isobaric curves, the system efficiency increases and decreases for wet and dry fluids, respectively, and the isentropic fluid achieves an approximately constant value for high turbine inlet temperatures. For dry working fluids, when the pressure is high, overheating can increase system efficiency by small degree. Hung et al. [41] argued the property of dry or isentropic fluids would reduce the area of net work in the *T*–*s* diagram. The second law efficiency would decrease with turbine inlet temperature due to the increased irreversibility [4,42]. As it was found the cycle thermal efficiency is a weak function of the turbine inlet temperature, it was recommended it is not necessary for organic fluids to be superheated [4,5,42,43]. Consequently, the

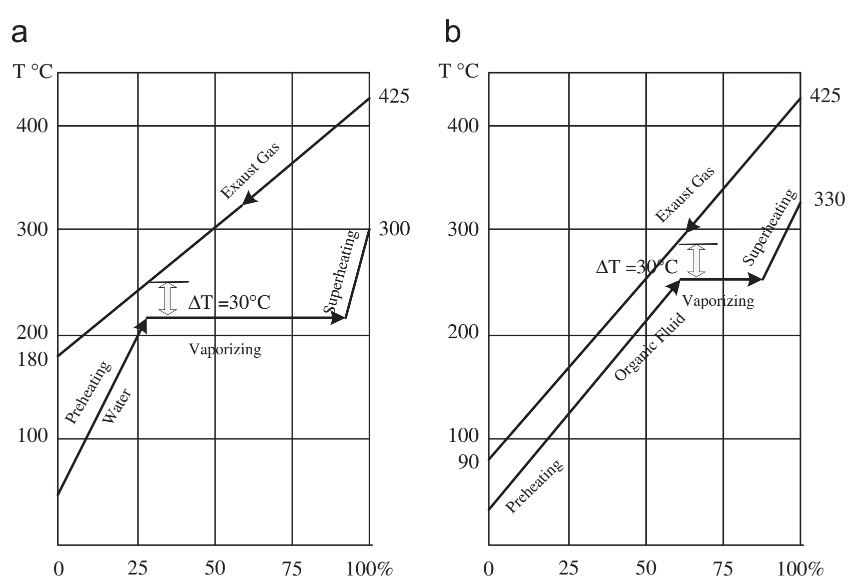

Fig. 2. The effects of vaporization latent heat on the irreversibility in the heat transfer process [48].

optimum efficiency of ORC working with a dry fluid could be achieved when the fluid operates along the saturation curve without being superheated [42,44,45].

2.1.2. The thermodynamic and physical properties

The performance of ORC systems strongly depends on working fluids' properties, which affects system efficiency, operating conditions, environmental impact and economic viability [3,46]. The relationships between working fluid properties and the ORC common economic and thermodynamic performance criteria from a theoretical and analytical point of view are discussed as follows:

2.1.2.1. Vaporization latent heat. The thermal efficiency of an ORC system can be written as [4,8]

$$\eta_I = \frac{W_{\text{net}}}{Q_{\text{in}}} \tag{1}$$

where W_{net} is the net output work and Q_{in} is the input heat of the ORC system.

A study presented in [47] notes that high vaporization latent heat enables most of the available heat to be added during the phase change operation, hence avoiding the need to regulate the superheating and expansion of the vapor through regenerative feed heating in order to enable higher efficiency. From the point of view of output work, Chen et al. [3] found that fluids with higher latent heat produce larger unit work output when the temperatures and other parameters are defined. However, when the heat source is the waste heat, organic fluids with lower specific vaporization heat are preferred. Lower vaporization heat of the working fluid causes the heat transfer process in the evaporator to occur mostly at variable temperature. Therefore the temperature profile of the working fluid in the evaporator better follows the temperature profile of heating fluid in the heat source [48]. This means that the temperature difference between fluids in the heat exchanger is reduced as illustrated in Fig. 2, hence the irreversibility in the heat transfer process is decreased. In a word, for waste heat or geothermal binary plants, suitable but not large vaporization latent heat would result in better overall performance of ORC plants.

Regarding to vaporization latent heat, the ratio of vaporization latent heat and sensible heat influences the thermal efficiency and exergy efficiency of ORC extremely. From literature [49], it could be found that both high evaporation temperature and vaporization enthalpy ratio (the ratio of vaporization latent heat and sensible heat) would result in a high ORC efficiency. Through the thermodynamic derivation, Mikielewicz et al. [50] recommended a thermodynamic index, in which a Jacob number was defined. In fact, this Jacob number is very close to the ratio of vaporization latent heat and sensible heat. Moreover, Kuo et al. [51] recommended a figure of merit defined as:

$$\text{Figure\_of\_merit}(FOM) = Ja^{0.1}\left(\frac{T_{\text{cond}}}{T_{\text{evap}}}\right)^{0.8} \tag{2}$$

which combining the Jakob number, condensing temperature and evaporation temperature. Here, different from [50], this Jakob number was defined as $Ja = Cp^{*}dT/Hv$, where $Cp^{*}dT$ is the vaporization sensible heat and Hv is vaporization latent heat, that is the reciprocal of the ratio of vaporization latent heat and sensible heat. Their results showed that the smaller figure of merit that is a larger ratio of vaporization latent heat and sensible heat is, the larger thermal efficiency is, which explained the results of literature [49].

From the point of view of exergy efficiency which is defined as [8,52]

$$\eta_{II} = \frac{W_{\text{net}}}{E_{\text{in}}} \tag{3}$$

where W_{net} is the net output work and Q_{in} is the input exergy of the ORC system, it could be seen from the analysis of Stijepovic et al. [46] that smaller the ratio of vaporization latent heat and sensible heat is, the larger exergy efficiency is, and therefore, there are trade-offs when the ratio of vaporization latent heat and sensible heat is regarded as the optimum indicator for best working fluids. It should be pointed out that the thermal efficiency is more appropriate as the performance index for solar energy and biofuel [7,49], while the net work is more suitable as the performance index for waste heat and geothermal applications [53,54]. Then, exergy efficiency is a useful tool to account for the energy quality, which could be applied in every renewable applications for analyzing the system irreversibility.

2.1.2.2. Density. High vapor density is of key importance, especially for fluids showing a very low condensing pressure (e.g. silicon oils). A low density leads to a higher volume flow rate: the pressure drops in the heat exchangers are increased, and the size of the expander must be increased. This has a non-negligible impact on the cost of the system [3,55].

Under the assumption of neglecting any influence of Reynolds number, the isentropic efficiency can be expressed as a function of two parameters only [56]:

the size parameter

$$SP = \frac{\sqrt{\dot{V}_{out}}}{\sqrt[4]{\Delta H_{is}}} = \frac{\sqrt{\dot{m}_{out}/\rho_{out}}}{\sqrt[4]{\Delta H_{is}}} \tag{4}$$

which accounts for the actual turbine dimensions and the isentropic volume flow ratio

$$VFR = \frac{\dot{V}_{out}}{\dot{V}_{in}} = \frac{\rho_{in}}{\rho_{out}} \tag{5}$$

defined as the specific volume variation across the turbine in an isentropic process, which accounts for the effect of the compressibility through the expansion.

According to Macchi and Perdichizzi [56], a higher value of SP results in larger turbine size. From Eq. (4) it appears that a higher density at turbine outlet has a negative impact on SP and therefore turbine size will be smaller. Also based on Macchi and Perdichizzi

Table 1
Listing of specific work, total work of pump and liquid specific heat for selected working fluids [60](T_e=80 °C and T_c=30 °C).

Working fluids	w_p [kJ/kg]	W_p [kW]	C_{pl} [kj/kg/k]
Propylene	5.24	95.29	2.73
Propane	5.2	88.41	2.78
R1234yf	2.25	86.2	1.42
R227ea	1.37	62.13	1.20
R134a	1.91	59.59	1.45
R1234ze	1.78	54.18	1.40
RC318	0.96	43.37	1.13
R152a	1.96	39.74	1.83
R600a	2.47	34.82	2.46
R236fa	0.99	31.79	1.28
R236ea	0.76	22.07	1.27
R245fa	0.69	16.25	1.33
R245ca	0.47	10.32	1.34
MM	0.1	1.81	1.92
Cyclohexane	0.14	1.54	1.85
Benzene	0.11	1.22	1.75
Toluene	0.06	0.59	1.72
MDM	0.01	0.29	1.83

[56], lower values of VFR deliver higher turbine efficiency. Moreover, Invernizzi et al. [57] state that in order to achieve a turbine efficiency higher than 80%, the VFR should be lower than 50. Therefore a value for the ratio between densities at turbine inlet and outlet lower than 50 is better.

2.1.2.3. Specific heat. Liquid specific heat should be low so that it could decrease the work consumed by pump and increase the work output indirectly [3,58,59]. This are checked from the calculation results from Borsukiewicz-Gozdur [60] as shown in Table 1. From the results, we could find that there is not a direct relationship between specific work or total work of pump and liquid specific heat. For example, it can be seen that a larger value of C_{pl} leads to lower pump work for R236ea than that of R227ea. From the calculation expression for pump work as follows [60],

$$W_p = \dot{m}_f w_p = \dot{m}_f (P_e - P_c) v_l / \eta_p \tag{6}$$

it can seen that there is not direct relationship between specific work or total work of pump and liquid specific heat so a low liquid specific heat is not necessary according the pump work.

2.1.2.4. Critical temperature. Invernizzi et al. [61] thought that the turbine pressure expansion ratio is related to both the acentric factor and the critical temperature. If the condensation temperature and the ratio of evaporation temperature and condensation temperature are fixed, the pressure ratio increases with the acentric factor and the critical temperature. Meanwhile, for given evaporation and condensation temperatures, a cycle configuration of good efficiency is obtained only from fluids with a high critical temperature, although the system efficiency is a weak function of critical temperature [40]. This implies, however, a low condensation pressure which could conflict with turbine and plant design. Conversely a high condensation pressure, entailing a low T, is often in opposition to a good thermodynamic configuration [62]. Bruno et al. [63] considered the Aspen plus software library as their reference for the preliminary selected working fluids and the optimum high and low pressure of the saturated cycle maintaining the maximum first law efficiency of the cycle were found. The result shows that employing a fluid with higher critical temperature results in higher efficiency but lower condensing pressure. A complementary study is necessary to increase the condensing pressure of these working fluids to atmospheric pressure and repeat the simulation process to find the cycle efficiency at new working conditions. However, a high critical temperature also involves working at specific vapor densities much lower than the critical density. This reduced density shows a high impact on the design of the cycle, since the components need to be oversized [55].

2.1.2.5. Boiling temperature. Working fluids can be easy to handle at ambient environment, so the boiling temperature is expected to be 0–100 °C [1]. Mago et al. [42] determined the influence of the boiling point temperature (T_{bp}) on the system thermal efficiency for both basic and regenerative ORCs by comparing simulation results for R113, R123, R245ca and Isobutane. The results demonstrate that the fluid which shows the best thermal efficiency is the one that has the highest boiling point among the selected fluids. However, this study seemed to include only a small sample of working fluids and it is questionable if this result would hold across all fluids or different fluid family types.

According to the relations that Joback [64] reevaluated Lydersen's group contribution scheme for the critical properties as follows,

$$T_c = T_b [0.584 + 0.965\{\sum_k N_k (tck)\} - \{\sum_k N_k (tck)\}^2]^{-1} \tag{7}$$

where the contributions are indicated as tck and N_k is the group number, the boiling temperature is higher if the critical temperature is higher for a fluid in the same fluid family. But it's not true when fluids are not in the same fluid family. Based on Ref. [65], R236ea had a higher boiling point of 279.34 K than 272.66 K which is the boiling point of *n*-butane. From their results, R236ea had a larger thermal efficiency than *n*-butane, which means the best fluid is not the one that has the highest boiling point but it's true for the same fluid family based on other researcher's findings [66].

2.1.2.6. Freezing point. The freezing point of the fluid must be lower than the lowest temperature of the cycle.

2.1.2.7. Molecular weight. Expansion work tends to be in inverse relation to MW which means that turbines for heavy fluids tend to have a low peripheral speed and a small number of stages. In general complex molecules are also heavy and this characterizes most organics. If, as it often happens, a small work is associated with a large expansion ratio (for example in the range 100–1000) problems connected with supersonic flows, rather than specific work, are likely to influence the number of stages [62]. Furthermore, high molecular weight has a positive impact on turbine efficiency. However, fluids with high critical pressure and high molecular weight require higher heat transfer area [46].

2.1.2.8. Molecular complexity. Molecular complexity is defined as [61]:

$$\sigma = \frac{T_{CR}}{R}\left(\frac{\partial S}{\partial T}\right)_{\mathrm{SV}, T_r = 0.7} \tag{8}$$

From the definition of molecular complexity, it can be seen that it is directly related to whether a working fluid is dry, wet or isentropic. The qualitative effects of the molecular structure on the value of σ are easily highlighted in case of the saturated vapor is comparable to an ideal gas. In this case

$$\begin{aligned}\sigma &= \frac{T_{CR}}{R}\left[\left(\frac{\partial S}{\partial p}\right)_{\mathrm{T}}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{SV}} + \left(\frac{\partial S}{\partial T}\right)_{\mathrm{p}}\right]_{\mathrm{SV}, T_r = 0.7} \\ &= \frac{T_{CR}}{R}\left[-\frac{R}{p}\left(\frac{\partial p}{\partial T}\right)_{\mathrm{SV}} + \frac{C_P^0}{T}\right]_{\mathrm{SV}, T_r = 0.7} \\ &= \left[-\frac{1}{p_R}\left(\frac{\partial p_r}{\partial T_r}\right)_{\mathrm{SV}} + \frac{\gamma}{\gamma - 1}\frac{1}{T_r}\right]_{\mathrm{SV}, T_r = 0.7}\end{aligned} \tag{9}$$

For simple molecules the term $-(\partial p_r/\partial T_r)_{\mathrm{SV}}/p_R$ prevails on the positive term $\gamma/[(\gamma-1)T_r]$ and the slope of the saturated vapor line in the T–s plan is negative and this working fluid is wet. According to [61], if the molecular complexity increases, the heat capacity ratio γ decreases, tending to one, and the slope of the saturated vapor line becomes positive: the more positive, the more complex is the molecular structure. The slope of the vapor-mixture boundary is, to a first approximation, a function only of the number of atoms in the molecule, not of their weight or character [67,68]. As a rule, the critical temperature and the acentric factor of a fluid increase with the molecular complexity, while the critical pressure decreases with molecular complexity, this is true for homologous fluids. For homologous fluids, molecular complexity increases with the number of atoms in the molecule [61].

So the adiabatic expansion in turbine yields invariably superheated vapor conditions, where the extent of superheating is proportional to molecular complexity. Moreover, the greater molecular complexity, the less vapor cooling during the expansion. Through the preliminary design of the turbine, the lower molecular complexity, the less isentropic efficiency in the same turbine size [61]. At both temperature levels and based on all performance

Table 2
Pure working fluid candidates for ORC.

Category and name	Alt. name	P_c (bar)	T_c (°C)	Source
Hydrocarbons (HCs)				
Ethane	R-170	48.7	32	[3,8,58,105–107]
Propene	R-1270	45.3	91	[3,8,58,105–107] [3,9,66,105] [3,9,66,105]
Propane	R-290	41.8	96	[3,9,58,66,69,70,105,106,108–111]
Cyclopropane	HC-270	54.8	124	[3,58,66,112,113]
Propyne	–	56.3	129	[3]
Isobutane	R-600a	36.4	135	[3,7,9,42,53,54,58,63,66,69,105,106,108,109,111,114–120]
Isobutene	–	39.7	144	[7,65,106,121]
N-butane	R-600	37.9	152	[3,7,9,51,53,54,63,65,66,69,108,109,111–114,120–124]
Neopentane	–	31.6	160	[7,65,66,108,113]
Isopentane	R-601a	33.7	187	[7,40,54,63,65,66,108,110,112,113,115–117,119,121–123,125]
N-pentane	R-601	33.6	196	[3,7,40,51,53,54,63,66,69,70,83,108,109,112,121–123,126–130]
Isohexane	–	30.4	225	[7,121]
N-hexane	–	30.6	235	[7,54,63,65,66,109,119,121,127]
N-heptane	–	27.3	267	[7,54,63,110,127]
Cyclohexane	–	40.7	280	[7,54,63,69,119,129,131,132]
N-octane	–	25	296	[7,54,109,127]
N-nonane	–	22.7	321	[7,54,109,127]
N-decane	–	21.0	345	[7,54,127,132]
N-dodecane	–	17.9	382	[7,54,109,127]
Benzene	–	48.8	298	[3,4,7,37,40,41,110,121,127,133]
Toluene	–	41.3	319	[3,7,37,40,41,49,54,63,109,113,119,121,127,132,134–136]
p-Xylene	–	34.8	342	[37,40,136]
Ethylbenzene	–	36.1	344	[41,49,63,113,136]
N-propylbenzene	–	32	365	[49,63]
N-butylbenzene	–	28.9	388	[49,63,113,136]
Perfluorocarbons (PCFs)				
Carbon-tetrafluoride	R-14	36.8	-46	
Hexafluoroethane	R-116	30.5	20	[3,58]
Octafluoropropane	R-218	26.8	73	[3,7–9,63,66,107]
Perfluoro-*N*-pentane	PF-5050	20.2	149	[7,65,66,121,126]
Decafluorobutane	R-3-1-10	23.2	113	[3]
Dodecafluoropentane	R-4-1-12	20.5	147	[3]
Chlorofluorocarbons (CFCs)				
Trichlorofluoromethane	R-11	43.7	197	[4,9,40,41,54,112,114,124,133,137]
Dichlorodifluoromethane	R-12	39.5	111	[4,5,9,41,43,69,112]
Trichlorotrifluoroethane	R-113	33.8	213	[4,9,37,41,42,54,65,69,109,112,114,121,124,128,137]
Dichlorotetrafluoroethane	R-114	32.4	145	[9,41,54,69,112,124]
Chloropentafluoroethane	R-115	30.8	79	[9,107]
Hydroflurocarbons (HFCs)				
Trifluoromethane	R-23	48.3	26	[3,58,112]
Difluoromethane	R-32	57.4	78	[3,7,58,66,69,112]
Fluoromethane	R-41	59.0	44	[3,8,66,107]
Pentafluoroethane	R-125	36.3	66	[3,8,58,66,106,107,112]
1,1,1,2-Tetrafluoroethane	R-134a	40.6	101	[3–5,8,9,12,43,50,53,58,63,66,69,70,83,106–109,111,112,120,125,129,130,133,138,139]
1,1,1-Trifluoroethane	R-143a	37.6	73	[3,8,9,58,66,83,107,112]
1,1-Difluoroethane	R-152a	44.5	112	[3,8,9,41,53,58,66,69,106,108,109,111,112,120]
1,1,1,2,3,3,3-Heptafluoropropane	R-227ea	28.7	101	[3,7–9,53,65,66,70,105,108,115–117,139]
1,1,1,3,3,3-Hexafluoropropane	R-236fa	31.9	124	[7–9,51,53,65,66,83,105,118,129,131]
1,1,1,2,3,3-Hexafluoropropane	R-236ea	34.1	139	[3,7–9,53,63,65,66,112,114,120,121,124]
1,1,1,3,3-Pentafluoropropane	R-245fa	36.1	153	[3,7–9,51,53,54,65,66,70,83,105,109,112,115–125,129–131,140–144]
1,1,2,2,3-Pentafluoropropane	R-245ca	38.9	174	[3,7–9,42,53,66,109,113,114,118,120,121,124,145]
Octafluorocyclobutane	RC-318	27.8	114	[3,7,9,63,65,66,69,105]
1,1,1,2,2,3,3,4-Octafluorobutane	R-338mccq	27.2	159	[66]
1,1,1,3,3-Pentafluorobutane	R-365mfc	32.7	187	[7,50,121,131,139]
Hydrofluoroolefins (HFOs)				
2,3,3,3-Tetrafluoropropene	HFO-1234yf	33.8	94.7	[9,125,129]
Hydrochloroflurocarbons (HCFCs)				
Dichlorofluoromethane	R-21	51.8	178	[3,58,112,123]
Chlorodifluoromethane	R-22	49.9	96	[3,9,58,106,112]
1,1-Dichloro-2,2,2-trifluoroethane	R-123	36.6	183	[3,5,8,9,37, 40–43,50,51,53,54,58,69,70,106,109,112,114,117,118,121,122,124,126,128,137,142,145,146]
2-Chloro-1,1,1,2-tetrafluoroethane	R-124	36.2	122	[3,9,58,106,112]
1,1-Dichloro-1-fluoroethane	R-141b	42.1	204	[3,9,50,53,54,69,112,114,121–124,137,145]
1-Chloro-1,1-difluoroethane	R-142b	40.6	137	[3,9,53,54,58,106,112]
Siloxanes				
Hexamethyldisiloxane	MM	19.1	245	[63,113,134,135,147]
Octamethyltrisiloxane	MDM	14.4	291	[63,113,147]
Decamethyltetrasiloxane	MD2M	12.2	326	[63,113,147]
Dodecamethylpentasiloxane	MD3M	9.3	354	[83,113,136]
Octamethylcyclotetrasiloxane	D4	13.1	312	[134,135,147]
Decamethylcyclopentasiloxane	D5	11.6	346	[136,147]
Dodecamethylcyclohexasiloxane	D6	9.5	371	[136,147]
Alcohols				
Methanol	–	81.0	240	[54,69]

Table 2 (*continued*)

Category and name	Alt. name	P_c (bar)	T_c (°C)	Source
Ethanol	–	40.6	241	[40,50,54,69,117,125]
Fluorinated ethers				
Pentafluorodimethylether	RE125	33.6	81	[66]
Bis-difluoromethyl-ether	RE134	42.3	147	[63,66,112]
2-Difluoromethoxy-1,1,1-trifluoroethane	RE245	34.2	170	[63,66,112]
Pentafluoromethoxyethane	RE245mc	28.9	134	[66]
Heptafluoropropyl-methyl-ether	RE347mcc	24.8	165	[66]
Ethers				
Dimethyl-ether	RE170	53.7	127	[9,66]
Diethyl-ether	R-610	36.4	193	[63]
Inorganics				
Ammonia	R-717	113.3	132	[3,4,9,12,43,54,69,107,108,110,114,117,120,126,148]
Water	R-718	220.6	374	[3,4,69,110,111,114,127,131]
Carbon dioxide	R-744	73.8	31	[3,8]

factors higher molecular complexity results in a more effective regenerative cycle. The only exceptions to this rule are Benzene and Cyclohexane. This means that the regeneration will be more effective in ORCs employing high molecular complexity working fluids if they are not Cyclohydrocarbons [7]. However, for waste heat or geothermal binary plants, the greater molecular complexity, the less system efficiency and work output [61]. In brief, select working fluids according to molecular complexity should be based on the type of heat source.

2.1.2.9. Viscosity. A low viscosity both in the liquid and vapor phases is required to maintain low friction losses in the heat exchangers and pipes.

2.1.2.10. Conductivity. High conductivity is required to obtain a high heat transfer coefficient in the heat exchangers.

2.2. Review of pure working fluids' screening

Due to working fluid selection is so important for ORC system performance and economy that many researchers have carried on working fluid screening. The screening method is by far the most used method for fluid selection in the scientific literature: it consists in building steady-state simulation model of the ORC cycle and run it with different working fluids [55]. Table 2 exhibits pure working fluid candidates for organic Rankine cycle, it can be seen that all kinds of organic fluids and inorganics could be used in a ORC system. From the structural point of view and type of atoms in the fluid molecule, the ORC working fluids can be categorized under seven main classes:

1. Hydrocarbons including linear (*n*-butane, *n*-pentane), branched (Isobutane, Isopentane), and aromatic hydrocarbons (Toluene, Benzene) have:
    - Desirable thermodynamic properties
    - Flammability issues
2. Perfluorocarbons (fully fluorinatedhydrocarbons) are/have:
    - Extremely inert and stable
    - Extreme molecular complexity
    - Thermodynamically undesirable
3. Siloxanes (MM, MM/MDM/MD2M)
    - Attractive for a mix of physical and thermal properties (low toxicity and flammability level; high molecular mass; prolonged use as a high temperature heat carrier)
    - They are often available as mixtures rather than as pure fluids
    - Isobaric condensation and evaporation are not isothermal and exhibit a certain glide
4. Partially flouro-substituted straight chain hydrocarbons
    - There are several zero ODP fluids among them which are of considerable potential interest
5. Ethers and fluorinated ether, have:
    - Flammability and toxicity issues
    - Thermodynamically undesirable
6. Alcohols, have:
    - Flammability issues
    - Soluble in water
    - Thermodynamically undesirable
7. Inorganics, have:
    - Extensive and inexpensive
    - Small environmental impact
    - Some operation problems

Table 3 summaries the recommended fluids for different applications, working conditions and performance indicators. From Table 2, it can be seen that despite the multiplicity of the working fluid studies, no single fluid has been identified as optimal for the ORC. This is because:

1. The extent of fluid candidates varies. Chen et al. [3] considered 35 pure working fluid candidates, Tchanche et al. [69] investigated 20 working fluids and Saleh et al. [66] screened from 31 pure fluids.
2. Different types of heat source and working conditions leading to different optimal working fluids. Lakew et al. [70] concluded that R227ea produces the highest power for heat source temperature range considered here (80–160 °C), while R245fa gives higher work output for temperature greater than 160 °C.
3. Different performance indicators result in different best working fluid. Zhang et al. [8] found that Fluids favored by the thermal efficiency and exergy efficiency are R123, R600, R245fa, R245ca and R600a. High recovery efficiency is obtained for R218, R125 and R41. Low APR value is presented for R152a, R134a, R600 and R143a. Low LEC value is observed for R152a, R600, R600a, R134a, R143a, R125 as well as R41.

While fluid selection studies in the scientific literature cover a broad range of working fluids, only a few fluids are actually used in commercial ORC power plants. These fluids are the following, classified in terms of critical temperature [55]:

HFC-134a: Used in geothermal power plants or in very low temperature waste heat recovery.

HFC-245fa: Low temperature working fluid, mainly used in waste heat recovery.

N-pentane: Used in the only commercial solar ORC power plant in Nevada. Other applications include waste heat recovery and medium temperature geothermy.

Table 3
Recommended fluids for different applications, working conditions and performance indicators.

Applications	Heat source temperature	Evaporation temperature	Condensation temperature	Performance indicators	Recommended fluids	Source
WHR	-	67–287 °C[a]	20 °C	First law efficiency	Benzene	[4]
WHR	327 °C	-	20–60 °C	First law efficiency Total irreversibility	*p*-Xylene	[37]
WHR	-	80–110 °C	35–60 °C	First law efficiency	R123, R124	[106]
WHR	-	100–210 °C[b]	25 °C	First law efficiency Second law efficiency Total irreversibility	R113	[42]
WHR	145 °C	80–140 °C[c]	20 °C	Work output	R236ea	[114]
WHR	140 °C	-	27 °C	Work output First law efficiency	R123	[5]
WHR	470 °C	96–221 °C	35 °C	First law efficiency	Benzene	[133]
WHR	100–250 °C	80–230 °C	30 °C	First law efficiency	Benzene	[110]
WHR	250–500 °C	Te[d]	85 °C	First law efficiency	*n*-hexane, *n*-pentane for 250 °C toluene, *n*-octane, andwater for 350 °C toluene and *n*-dodecane for 500 °C	[127]
WHR	85 °C	55–80 °C	25 °C	First law efficiency Second law efficiency Total irreversibility Work output	Butane,R245fa and R141b,	[123]
WHR	85 °C	60 °C	25 °C	First law efficiency	R123	[118]
WHR	160 °C	144–156 °C	20 °C	A/Wnet[e]	R11	[137]
WHR	150 °C	-	20 °C	Work output UA[f] and SP[g]	R114, R245fa, R601a, R601, R141b and R113	[54]
WHR	140 °C	-	20 °C	A multi-objective criteria included A/Wnet and heat recovery efficiency	R123 for 100–180 °CR 141b for higher than 180 °C	[53]
WHR	292 °C	277 °C	27 °C	First law efficiency Second law efficiency Work output	R123	[43]
WHR	327 °C	Te[h]	27–87 °C	First law efficiency Total irreversibility	R245fa, R245ca	[124]
Geothermal	80–115 °C	65–100 °C	25 °C	First law efficiency Work output	Propene	[105]
Geothermal	70–90 °C	-	-	A/Wnet	Ammonia	[126]
Geothermal	120 °C	100 °C	30 °C	First law efficiency	RE134, RE245, R600, R245fa, R245ca, R601	[66]
Geothermal	91.1 °C	Te[i]	28 °C	First law efficiency Second law efficiency A/Wnet	R601a, R601	[122]
Biomass	–	250–350 °C	90 °C	First law efficiency	Butylbenzene	[49]
Biomass	–	170 °C	50 °C	First law efficiency	Ethanol	[50]
Solar	–	60–100 °C	35 °C	First law efficiency Second law efficiency Total irreversibility	R134a	[69]
Solar	–	70– (T_C−10) °C	30 °C	A/Wnet	R245fa	[108]
Solar	–	120–150 °C	15 °C	First law efficiency	Solkatherm	[130]
–	–	80–200 °C	20 °C	First law efficiency Exergy efficiency	R227ea for 80–160 °CR245fa for160–200 °C	[70]
–	60–160 °C	55–155 °C	30 °C	First law efficiency Second law efficiency	Hexane	[65]

[a] Turbine inlet temperature corresponding to 2.5 MPa.
[b] Turbine inlet temperature corresponding to 2.0 MPa.
[c] Turbine inlet temperature.
[d] Evaporation temperature corresponding to evaporation pressure of 0.5–2 MPa.
[e] The ratio of total heat transfer area to net power output.
[f] The total heat transfer capacity.
[g] The expander size parameter.
[h] Evaporation temperature corresponding to evaporation pressure of 0.2–2 MPa.
[i] Evaporation temperature corresponding to evaporation pressure of 0.15–0.6 MPa.

Solkatherm: Waste heat recovery.
OMTS: CHP power plants.
Toluene: Waste heat recovery

According to Wang et al. [71], the optimal selections of working fluids corresponding to the heat source temperature level are shown as Fig. 3.

In a word, there is not a working fluid suitable for any organic Rankine cycle system. At the same time, the working fluid selection should not only consider the thermodynamic performance (the first law of thermodynamics, output power, etc.) and the system economy, but also consider other factors, such as the

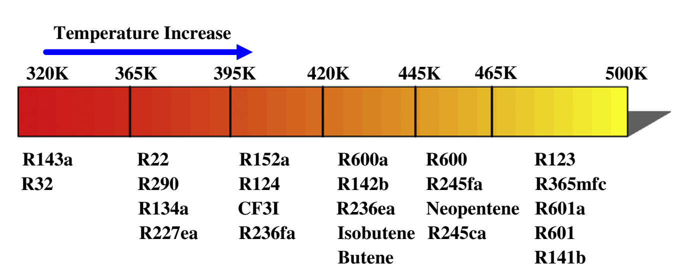

Fig. 3. The optimal selections of working fluids corresponding to the heat source temperature level [71].

maximum and minimum bearable temperature and system pressure, expanders or turbines design and environmental and safety considerations, which will be further discussed in Section 2.4.

2.3. Review of mixed working fluids' screening

Because of a varying temperature for the heat source of waste heat or geothermal binary plants, the thermal performances of such cycles are quite poor, since pure fluids have the properties of boiling and condensing at constant temperature, which leads to large temperature differences in the vapor generator and condenser and in turn inevitably increases the irreversibility. A major advantage for using mixtures as a working fluid in the power generation systems instead of pure working fluids is that heat can be supplied or rejected at variable temperature but still at constant pressure, since the boiling temperature now varies during the phase change and the binary mixture evaporates over a wide range of temperature. The variable-temperature heat transfer process alleviates the temperature mismatch between hot and cold streams in heat exchanging components of the system, which then reduces the exergy destruction in the power cycles [72,73]. Kim et al. [74] comparatively analyzed ammonia–water based Rankine (AWR) and regenerative Rankine (AWRR) power generation cycles by investigating the effects of ammonia mass concentration in the working fluid on the thermodynamic performances of systems. The results show that the characteristics of temperature distributions of the fluid streams in the heat exchangers vary quite complicatedly and sensitively with changing ammonia concentration and they show the benefit of using binary working fluid by minimizing the temperature differences of fluid streams in the heat exchangers. The researches about zeotropic mixture ORC are increasing, but it's still limited. Table 4 gives a summary of working fluids and cycle types for zeotropic mixture ORC.

While transcritical Rankine cycle using a pure working fluid does overcome the pinch point limitations of ORCs during the heating process, the condensation process is still isothermal. Chen et al. [75] came up with a concept of zeotropic transcritical Rankine cycle and their results showed that a transcritical cycle

Table 4
Summary of mixture ORC.

Working fluids and their fractions	Cycle types	Comments	Source
MM 3.18% MDM 34.14% MD2M 45.51% MD3M 16.17% MD4M 1.00%	Saturated ORC Superheated ORC Transcritical ORC	Both the temperature drop and profile depend on the nature, number and difference in critical temperatures of mixture constituents and on the mixture composition	[76]
R22 70% R114 30%	Saturated ORC	The turbine expansion ended in the wet vapor region. If the temperature difference is reasonably large, then it is possible to preheat the compressed liquid by recovering a fraction of the heat of condensation of the vapor in a condensing regenerator	[76]
Propane 50% *n*-Pentane 50%	Superheated ORC Transcritical ORC	Primary heater-temperature profiles feature almost uniform heat absorption, which implies very good matching with sensible heat sources	[76]
Propane 1.0/0.9/0.8/0.7/0.6/0.5 Ethane 0/0.1/0.2/0.3/0.4/0.5	Superheated ORC	For similar efficiencies (10.9–9.9%) for different mass compositions of propane–ethane mixture obtained have been different values of power (182.3–231.2 kW)	[105]
R401A, R401B, R401C	Superheated ORC Saturated ORC	The small recovery system performance of the working fluid blend R-401C is due to the strict thermal operative conditions imposed	[47]
MM 60% MDM 30% MD2M 10%	Saturated ORC	The overall performance is comparable to the considered pure fluids if the mean condensation temperature is the same, but it could be even better if air cooling is considered	[62]
R141b 0.9/0.8/0.7/0.6/0.5/0.4/0.3 RC318 0.1/0.2/0.3/0.4/0.5/0.6/0.7	Superheated ORC	The mixture ORC does have lower efficiency than pure-fluid ORC, but to the ORC with IHE, the mixture may have better performance than the pure-fluid	[78]
R32 30% R134a 70%	Transcritical ORC	It was found that the SRC using a zeotropic mixture of 0.7R134a/0.3R32 can achieve thermal efficiency of 10.77–13.35% with the cycle high temperature of 393–453 K as compared to 9.70–10.13% from an ORC using pure R134a working fluid under the same thermal conditions	[75]
R245fa 0.9/0.65/0.45 R152a 0.1/0.35/0.55	Saturated ORC Superheated ORC	The main benefits of the mixtures were that the cost of the cycle could be reduced as smaller expanders are suited and that the range of usable fluids increased	[6]
R245fa 0.9/0.7 R152a 0.1/0.3	Superheated ORC	In the experimental superheating period, the average power output of R245fa/R152a (0.7/0.3) is higher than that of pure R245fa by 29.10%. It can be seen that the power output varies accordingly and the system capacity adjustment could be easily realized under different composition of zeotropic mixtures	[77]
Isobutane/Isopentane R227ea/R245fa	Saturated ORC	The results show that the non-isothermal phase change of mixtures leads to an efficiency increase in comparison to pure fluids	[52]
R245fa-R365mfc R245fa-isopentane Isobutane-isopentane R245fa-pentane Isopentane-isohexane Pentane-hexane Isopentane-cyclohexane Isopentane-hexane R245fa-isopentane-isohexane R245fa-pentane-hexane Isopentane-isohexane-cyclohexane	Saturated ORC	An increase in cycle efficiency, for binary mixtures, of 15.7% and an increase in generated electricity of 12.3% is found possible for heat source and ORC cycle parameters for a lower temperature source (150 °C). The potential for efficiency and electricity production increase is less pronounced (6.0% and 5.5%, respectively) for a heat source type at a higher temperature (250 °C). In the considered cases, the addition of a third component to a binary mixture has only a small effect	[72]
R125/R134a 0.799/0.201 R125/R227ea 0.803/0.197 R125/R236ea 0.940/0.060 R125/R245fa 0.939/0.061	Transcritical ORC	Under the simulation conditions of the present study, the optimized R125/R245fa mixture transcritical cycle yielded 11% more power than did the optimized R134a subcritical cycle	[73]
R245fa/Isopentane 0.3/0.7	Superheated ORC	It can be concluded that the mixture chosen here gives as good a performance as individual components and yet obviating the negative points of flammability of isopentane and high GWP of R-245fa	[149]

using a zeotropic mixture of 0.7R134a/0.3R32 can achieve a performance improvement of 10–30% over the ORC using pure R134a working fluid in the same thermal conditions. Although early studies assumed that a zeotropic mixture improved transcritical cycle's condensing process, Baik et al. [73] found its impact insignificant. However, to some extent, that is the result of a constant cooling water mass flow rate. Both the temperature drop and profile depend on the nature, number and difference in critical temperatures of mixture constituents and on the mixture composition [76]. Although no general rule can be given to predict these characteristics, it was found empirically that mixtures of 3 or more components in similar proportions exhibit almost constant apparent heat capacity during condensation, which allows good matching to the requirements of sensible heat uses (district heating, sanitary water production, etc., see Fig. 4a). On the other hand, two-component mixtures with a marked composition imbalance produce large variations in apparent heat capacities with unfavorable temperature profiles (Fig. 4b).

In general, mixtures permit a higher variety concerning the choice of working fluid for ORC power plants. Additionally, a variation in mixture composition can be used to adjust physical, environmental, safety and chemical properties of the working fluid or to improve design parameters of cycle components [52]. Due to the non-isothermal phase change for zeotropic mixture, when temperature glide is large, it could reclaim the latent heat of condensing partly to preheat working fluids, and then, the system efficiency will increase [6,76]. When adopting air cooling, the condensing process of zeotropic mixture ORC could reduce both cooler frontal area and fan power consumption [76]. Furthermore, when using zeotropic mixture as working fluids, it could reduce the sizes of equipment. Wang et al. [6] compared three different mixture compositions of dry R245fa and wet R152a to pure R245fa and the main benefits of the mixtures were that the cost of the cycle could be reduced as smaller expanders are suited.

At the respect of the mixture ORC's efficiency, the results in [72] are inconsistent in [77]. From the results of Angelino et al. [76], Li et al. [78] and Wang et al. [6], the efficiency of zeotropic ORC was lower than that of pure working fluid ORC. However, their conclusions have limits. In the research of Angelino et al. [76], the efficiency of zeotropic ORC was compared with pure working fluid ORC with compositions different from zeotropic mixtures; in the study of Li et al. [78], the flow rate of working fluids was fixed, which would lead to different evaporation temperatures, so that it is unfair considering Carnot theory; in the comparison of Wang et al. [6], the constant variable is the turbine inlet temperature but not evaporation temperature.

Because the mixing rule of zeotropic mixture is rather complicated [3], it's a tough job to determine the optimum compositions and their fractions. Based on the research of refrigeration, Chys et al. [72] provided the method of screening compositions for zeotropic mixtures, which is very favorable for preliminary determination of zeotropic mixture. But for a given heat source temperature, the means of determining the best compositions and fractions need further research. Moreover, the information about heat-transfer coefficients (which are known to be strongly affected by mixture properties) should be obtained [76]. Leakages present a larger problem than is the case for pure fluids, especially in the evaporation stage [72].

2.4. Limitation of working fluid selection

2.4.1. Limitation of evaporation and condensing pressure

As the higher pressure ratio leads to a higher efficiency, it's prefer to expand higher and lower pressure limits of the cycle, but there are always some practical restrictions [7]. The limitations of evaporation and condensing pressure in literatures are summarized in Table 5. Previous works have sometimes considered as maximum pressure for the working fluid 20 bar or the vapor pressure at T_{max}. The 20 bar limit arose from legal prescriptions in some countries known as “Dampfkesselverordnung (steam boiler code)” [79]. It is better that the condensing pressure is higher than atmospheric pressure so that it could avoid cool air leakage into system which would reduce system efficiency. The lowest condensing pressure adopted by condenser is 5 kPa according to [16].

Near critical pressure, small changes in temperature are equivalent to large changes in pressure that make the system unstable. In addition to this, if the slope of the saturated vapor curve on the *T–s* diagram is steep enough, the fluid will cross the two-phase dome initially during expansion and then end up in the superheated vapor state at the end of the expansion as shown in Fig. 5. Therefore a reasonable distance between the higher limit of the cycle and the critical point of the fluid should be considered [7]. The author gave the method of determining the limit of the highest evaporation pressure. As seen from Fig. 5, the slope of the temperature-entropy diagram has been used to determine the higher limit of the Rankine cycle in this study. To avoid the presence of liquid in every single section of the turbine, the highest input pressure of the turbine is the pressure that the slope of temperature-entropy diagram is equal to infinity at that point (point “A” in Fig. 5). Calculating the higher pressure and temperature limit of the cycle based on this criterion shows that for most of fluids a large capacity of producing power is neglected. Based on

Table 5
The limitations of evaporation and condensing pressure in literatures.

Maximum evaporation pressure	Minimum condensing pressure	Source
2.5 MPa	–	[58]
2.0 MPa	0.05 MPa	[49]
2.0 MPa	–	[66]
2.5 MPa	0.1 MPa	[69]
0.9 Pc	–	[116]

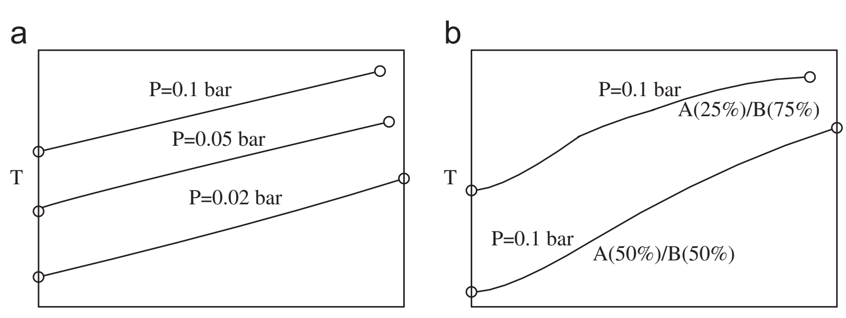

Fig. 4. Temperature profiles at different condensation pressures for a multi-component mixture. The quasi-linear behavior (a) provides good matching while the s-shape in two-component mixtures (b) are unfavorable [76].

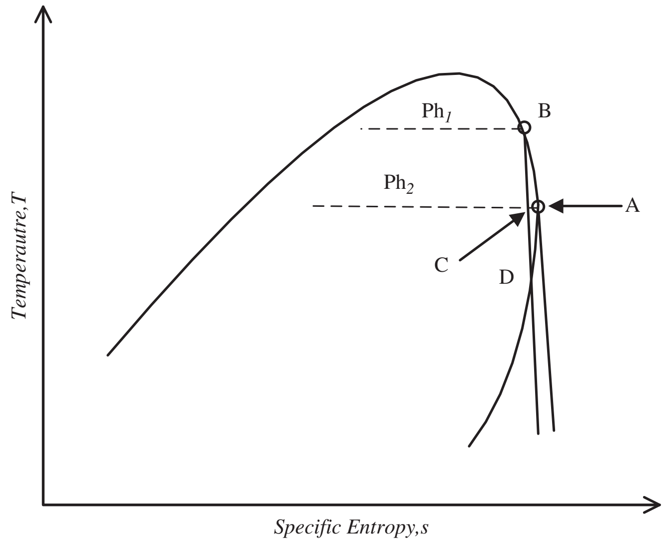

Fig. 5. Higher pressure limit of the ORC [7].

Table 6
Practical limits of the ORC for preselected working fluids [7].

Working fluid	Maximum P_{eva} (MPa)	Maximum T_{eva} (°C)	Minimum P_{con} (kPa)	Minimum T_{con} (°C)
Acetone	3.379	213	30.7	25
Benzene	4.067	274	12.7	25
Butane	3.013	138	234.7	25
Butene	2.808	125	297.2	25
C4F10	2.057	107	268.3	25
C5F12	1.803	141	84.7	25
Cis-butene	3.035	142	213.7	25
Cyclohexane	3.665	272	13	25
Decane	1.896	337	5.1	85
Dodecane	1.723	381	5.1	121
E134	2.747	125	212.8	25
Heptane	2.41	258	6.1	25
Hexane	2.68	226	20.2	25
Isobutane	2.89	121	350.5	25
Isobutene	2.877	125	305	25
Isohexane	2.682	216	28.2	25
Isopentane	2.887	177	91.8	25
Neopentane	2.788	152	171.4	25
Nonane	2.059	314	5	65
Octane	2.2	287	5	44
Pentane	2.865	186	68.3	25
R218	1.899	57	867.5	25
R-227ea	2.352	91	455.2	25
R-236ea	2.955	132	205.9	25
R-236fa	2.288	108	272.4	25
R-245ca	2.951	158	100.8	25
R-245fa	2.817	140	149.4	25
R-365mfc	2.712	177	53.4	25
R-C318	2.314	106	312.5	25
Toluene	3.576	307	5.1	31
Trans-butene	2.906	136	234.1	25
R-413A	1.839	59	720.2	25
R-423A	2.966	90	598	25
R-426A	1.562	55	687.8	25

this method, Table 6 shown the practical higher and lower limit of the cycle for each working fluid. Furthermore, the highest pressure should take the cost of equipments into consideration.

Regarding to the limitations of evaporation and condensing pressure, it could be used to conduct the preliminary screening of working fluids. For example, as in Table 6, in order to ensure the limitation of condenser pressure higher than 5 kPa, the condensing temperature of Dodecanese must increase to 121 °C, so that this fluid is not suitable for low-temperature applications.

2.4.2. *Limitation of the highest decomposition temperature*

The turbine inlet temperature could be close to flame temperature, but organic fluids would become chemically unstable. Therefore, maximum process temperature is limited to about 600 K [49]. Different from water, this must be considered in operation of ORC. Andersen and Bruno [80] presented a method to assess the chemical stability of potential working fluids by ampule testing techniques. The method allows the determination of the decomposition reaction rate constant of simple fluids at the temperatures and pressures of interest.

2.4.3. *Limitation of expansion machines*

The choice of working fluids has a strong connection to the types of expansion machines used in ORC system. In a certain condition, when a working fluid is selected, not all types of expansion machines are suitable for the imposed working conditions, and it needs the further design of expanders. However, because of inherent limitation of different types of expanders, working fluid selection should be determined by combining with the limitations of expansion machines.

For Radial inflow turbines, it exists several limited parameters, such as tip speed, rotating speed, specific speed and maximum Mach number in the turbine nozzle and rotor etc [55]. As a general rule, a high tip speed is always preferred since it increases the stage specific work. It is however limited by the strength of materials at the wheel periphery. Because of the influence of bearing capacity and loss, it exists an optimum rotating speed corresponding to the maximum efficiency. In order to obtain better isentropic efficiency, specific speed varies between 0.3 and 0.9. The maximum Mach number in the rotor is to avoid any local choking of the flow. A maximum Mach number of 0.85 is generally recommended in order to avoid any local choking of the flow in the rotor. The maximum Mach number in the turbine nozzle restrains the maximum allowable pressure/volume ratio over the turbine. A too high Mach number might decrease the efficiency and should be avoided.

For positive-displacement expanders, they are mainly limited by internal built-in volume ratio and swept volume [55]. The maximum internal built-in volume ratio of positive-displacement expander is usually not higher than 5. It is limited by the length of the rotor (bending stresses) in the case of a screw expander and by the number of spiral revolutions in the case of a scroll expander. The second main limitation of volumetric expanders is the swept volume. This swept volume is linked to the maximum rotor diameter in the case of screw expanders (about 400 mm) or to the maximum spiral height and diameter in the case of a scroll expander.

In the doctoral dissertation of Quoilin [55], the limitations described in the previous sections can be used to build a map of the allowable working conditions in a T_{ev}/T_{cd} diagram, as shown in Fig. 6, which shows the advantage of setting limits on the component size and therefore it does not lead to unrealistic working fluids. However, the operating maps of different working fluids are often overlapping, which means that this method must therefore be considered as preselection tool only.

2.4.4. *Limitation of environment and safety*

As to the environmental aspects, the main concerns include the ozone depletion potential (ODP), global warming potential (GWP) and the atmospheric lifetime (ALT). The ODP and GWP represent substance's potential to contribute to ozone degradation and globe warming. Due to environmental concerns, some working fluids

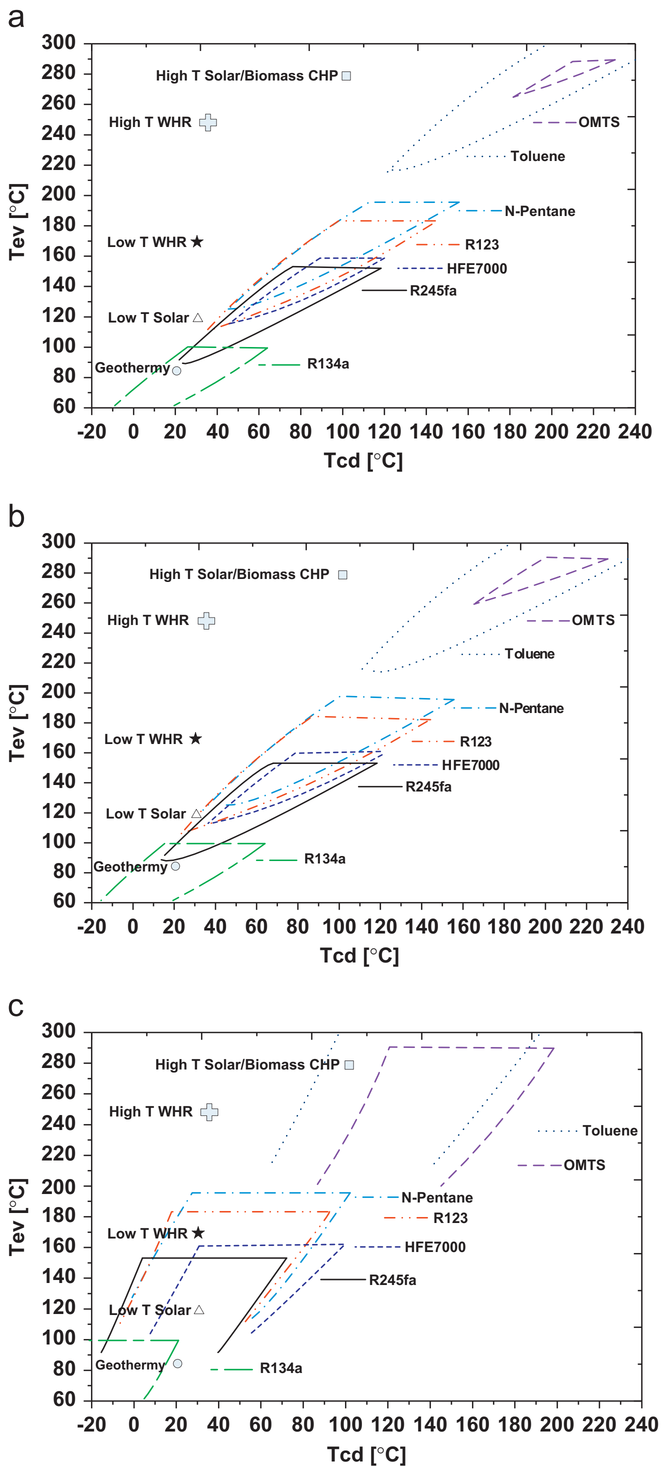

Fig. 6. Expansion machines' operating maps [55]. (a) Scroll expander, (b) Screw expander and (c) Radial inflow turbine.

have been phased out, such as R-11, R-12, R-113, R-114, and R-115, while some others are being phased out in 2020 or 2030 (such as R-21, R-22, R-123, R-124, R-141b and R-142b). In the working fluids primary selection those phased-out Substances may be not included according to the policy.

The ASHRAE refrigerant safety classification is a good indicator of the fluid's level of danger. Generally, characteristics like non-corrosive, non-flammable, and non-toxic are expected. But they are not always practically satisfiable or critically necessary. Many substances, like R-601, are considered flammable but this is not a problem if there is no ignition source around. However, autoignition is a problem, in particular for longer alkanes at temperatures above 200 °C. The maximum allowable concentration and the explosion limit should also be under consideration [1,3,59,81].

3. Expansion machines

Limiting the ORC system efficiency, an expander is a critical component in a relatively efficient and cost-effective ORC system. Expanders, in general, can be categorized into two types: One is the velocity type, such as axial turbine expanders; the other is the volume type, such as screw expanders, scroll expanders and reciprocal piston expanders [82].

3.1. Turbine

Turbines used in the ORC system, basically, have no difference from steam turbines. However, because of the large difference on the thermal physical property between organic fluids and steam, turbines used in the ORC system have some special characteristics as follows:

1) Organic fluids have the bigger molar mass so that their sound velocity is lower than steam. In the design process, it should avoid appearing supersonic in the nozzle outlet as far as possible, which causes additional shock loss;
2) For a certain temperature difference, turbines used in the ORC system have a higher expansion ratio and a smaller enthalpy drop than steam, especially in the low grade heat energy recovery, so that it will be affected by all kinds of losses;
3) Organic fluids have larger density and smaller specific volume than water, and the flow passage and overall dimensions of turbines can be smaller. In addition, because of the positive saturated vapor curve slope, the turbine exhaust vapor is still superheated, which can reduce the moisture vapor loss;
4) Organic turbines have compact layouts and small sizes so that it must pay attention to overspeed problem of a turbine during the load shedding;
5) Some of organic fluids are inflammable, explosive or expensive, and taking safety or the economy into consideration, it must strictly prevent working fluids leakage into air. For organic turbines, the sealing medium is gas and it's generally beneficial to adopt double-face seal.

While one-stage axial turbines are commonly used in systems with high flow rates and low pressure ratios, one-stage radial inflow turbines are suitable for use in systems with lower flow rates but higher pressure ratios, which makes them attractive propositions for ORC systems. There are advantages for selecting radial inflow turbines [83]:

1. Through minor modifications standard radial inflow turbines can be optimized for different geothermal resources.
2. They enable to smooth the seasonal variations by maintaining high efficiency levels at off-design conditions through the use of variable inlet guide vanes.
3. Radial inflow turbines are less sensitive to blade profile inaccuracies than axial turbines, which enable high efficiencies to be maintained as size decreases.
4. Radial-inflow turbines are more robust under increased blade road caused by using high-density fluids as either subcritical or supercritical conditions.
5. Radial inflow turbines are easier to manufacture relative to axial turbines as the blades are attached to the hub. The rotor

dynamic stability of the system is also improved due to a higher stiffness.

Fiaschi et al. [84] presented a reliable preliminary design of ORC radial expanders and the comparison of different working fluid behavior. Results showed that of the considered working fluids, R134a had the highest efficiency of 0.85. Li et al. [85] presented a quantitative study on the convection, radiation, and conduction heat transfer from a kW-scale expander. The prototype experimental researches of radial inflow turbines are summarized in Table 7.

3.2. Scroll expander

Common to all positive displacement devices, the scroll expander has a fixed volumetric ratio. The fixed built-in volume ratio can generate two types of losses if the system specific volume ratio is not equal to the expander nominal volume ratio: under-expansion and over-expansion. These two effects can considerably reduce the efficiency of the expansion process, the most common being the under-expansion. As a consequence, volumetric expanders are generally less adapted to high expansion ratios than turbomachines. Other sources of losses include friction losses, supply pressure drop, internal leakage and heat transfer [86,87]. Generally speaking, piston expanders are more appropriate for applications with large expansion ratio because their design allows for higher internal built-in volume ratios [55].

Compared to the other positive displacement expansion devices, the scroll expander has the most complicated geometry. Scrolls can be categorized into two types: compliant and kinematically constrained. Compliant scrolls require lubrication to operate efficiently without causing significant wear. Constrained scrolls in contrast can operate without lubrication. Another advantage of this device is that it does not require inlet or exhaust valves which reduces noise and improves the durability of the unit [88] and furthermore the relative rolling motion of the contact points offers less resistance than sliding friction. Additionally, the rolling contacts provide a seal such that large volumes of oil used as a sealant are not required and the leakage is reduced. The scroll expander can start under any system load without any start components.

Lemort et al. [86] presented the results of an experimental study carried out on a prototype of an open-drive oil-free scroll expander integrated into an ORC working with refrigerant R123. The results pointed out that the internal leakages and, to a lesser extent, the supply pressure drop and the mechanical losses are the main losses affecting the performance of the expander. Stefano Clemente et al. [89] recommended an ORC one-dimensional numerical model, which could calculate several main parameters, such as volume efficiency, isentropic efficiency etc. By combining a one-dimensional model of a scroll machine and a thermodynamic model with a whole ORC system, the authors evaluated how the performances are influenced by cycle parameters, scroll geometry and working fluid for different applications. The prototype experimental researches of scroll expanders are summarized in Table 7.

3.3. Screw expander

Screw expanders have been widely used as the expansion devices in Rankine cycle plants, especially for geothermal and waste heat applications.

The rotational speeds of the screw expanders are higher than the recommended operational speeds of some of the driven equipments, so that reduction gear boxes and speed control equipments might be required. Also, helical-screw expanders need a relatively high level of technology in their production. Lubrication of helical-screw machines is achieved principally by employing a working fluid/oil mixture as the lubricant between rotors, as well as the rotors and the casing. The lubrication problem in screw expanders is not as severe as in Wankel engines due to the relatively small, typically allowed running clearances (between the rotors and the casing) which do not lead to significant reductions in the machine efficiencies.

Table 7
The prototype researches of various types of expansion machines.

Researchers	Expander type	Working fluids	Isentropic efficiency (%)	Power [kW]	Rotate speed [rpm]	Pressure ratio
Yamamoto et al. [150]	Radial-inflow turbine	R123	48	0.15	17,000	–
Nguyen et al. [151]	Radial-inflow turbine	*n*-pentane	49.8	1.44	65,000	3.45
Yagoub et al. [152]	Radial-inflow	HFE-301	85	1.50	60,000	1.1
	turbine	*n*-pentane	40	1.50	60,000	1.3
Inoue et al. [153]	Radial-inflow turbine	TFE	70–85	5–10	15,000–30,000	4.8
Kang [154]	Radial-inflow turbine	R245fa	78.7	32.7	63,000	4.11
Pei et al. [155]	Radial-inflow turbine	R123	65	1.36	24,000	5.2
Li et al. [156]	Radial-inflow turbine	R123	68	2.40	40,000	6.3
Zanelli and Favrat [157]	Scroll expander	R134a	63–65	1–3.5	2400–3600	2.4–4.0
Mathias et al. [158]	Scroll expander	R123	67, 81, 83	1.2,1.38, 1.75	3670	8.8,5.5,3.1
Peterson et al. [159]	Scroll expander	R123	45–50	0.14–0.24	600–1400	3.28–3.87
Wang et al. [88]	Scroll expander	R134a	70–77	0.5–0.8	1015–3670	2.65–4.84
Saitoh et al. [160]	Scroll expander	R113	65	0–0.46	1800–4800	–
Kim et al. [161]	Scroll expander	Water	33.8	11–12	1000–1400	10.54–11.5
Manolakos et al. [162]	Scroll expander	R134a	10–65	0.35–2	300–390	–
Lemort et al. [86,87]	Scroll expander	R123	42.5–67	0.4–1.8	1771–2660	2.75–5.4
	Scroll expander	R245fa	45–71	0.2–2	–	2–5.7
Guangbin et al. [163]	Scroll expander	Air	–	0.4–1.1	1740–2340	3.66
Wang et al. [164]	Screw expander	Air	26–40	0.5–3	400–2900	–
Smith et al. [165]	Screw expander	R113	48–76	6–15.5	1300–3600	2.11
Baek et al. [166]	Reciprocating piston expander	CO_2	10.5	24.35	114	2.1
Zhang et al. [167]	Reciprocating piston expander	CO_2	62	–	306	2.4
Mohd et al. [101]	Rotary vane expander	R245fa	43–48	0.025–0.032	2200–3000	21.54–24.17
Yang et al. [102]	Rotary vane expander	CO_2	17.8–23	–	300–1500	–
Qiu et al. [168]	Rotary vane expander	HFE7000	52.88–55.45	1.66–1.72	841–860	2.063–2.095

Like all other positive displacement devices, the seal is critical to prevent internal leakage. In order to prevent direct contact but also achieve a seal between the lobes of each rotor in a screw expander, two methods of lubrication for different device types have been developed: oil injected and oil free. The oil injected type of machine is simple in mechanical design, cheap to manufacture, highly efficient, and widely used as a compressor. The oil free machine separates any oil from the working fluid by preventing contact between the rotors with lubricated meshing timing gears outside the working chamber. Internal seals are required against the bearings and chamber walls. These additional parts and requirements cause the oil free machine to be considerably more expensive than its oil injected counterpart.

Screw expanders depend on precise numerically-controlled machining to achieve a leak-resistance fit, especially with oil free types. Because of the tight sealing requirements, they tend to work better with wet fluids. A dry fluid system would still require seals that greatly increase the cost of the machine.

Smith et al. [90–92] have developed and investigated screw machines as expanders for over 20 years, including the researches about the modeling of screw expanders, performance prediction and experimental investigations etc. The prototype experimental researches of screw expanders are summarized in Table 7.

3.4. Reciprocating piston expander

Reciprocating piston expanders are widely used in the heat recovery of internal-combustion engine exhaust [93]. Previous study carried out by Teng et al. [94,95] indicated that steam/vapor turbine is restricted to steady-flow applications. Otherwise, if the heat addition is variable, the wetness in the late expansion stage may not be controllable. Due probably to above reasons, most of the Rankine engines for on-road-vehicle applications developed in past 30 years were the reciprocating engines.

Reciprocating pistons are complex devices that require precise timing of the intake and exhaust valves. They also require both primary and secondary balancing. Primary balance is the effect caused by a mass rotating about the shafts center and secondary is the effect of a mass that rotates around a center that is not concentric with the shaft. They are also known to have large friction losses from the large number of interacting surfaces. A primary contribution is friction between the piston rings, piston, and cylinder wall. An ORC could decrease the impact of these losses by dissolving oil into the working fluid.

However, reciprocating machines have some drawbacks;

- Torque pulsation is a common phenomenon due to the inherent discontinuity associated with the finite number of pistons or lobes and fixed displacement,
- Reliability is also an issue with positive-displacement machines because of a greater number of moving parts with the associated inherent balancing problems and in the case of pistons, a lubrication system to reduce leakage encountered in the gap between the moving seals and volute,
- Poor breathing characteristics due to the high fluid-friction losses across the valve systems,
- Lubrication difficulties, when operating with steam as the working medium
- High manufacturing costs.

Glavatskaya et al. [96] proposed a steady-state semi-empirical model of the reciprocating piston expander and the ambient and mechanical losses as well as internal leakage were taken into account by the model. Clemente et al. [97] also recommended the numerical model of a volumetric reciprocating expander, which was compared with the numerical model of scroll expander developed by the same author. Results showed that when working in the large expansion radio, reciprocating piston expanders had better performance than scroll expanders. The prototype experimental researches of reciprocating piston expanders are summarized in Table 7.

3.5. Rotary vane expander

Rotary vane expanders possess high tolerances for a wide range of vapor qualities of the working fluid, and also provide some additional advantages such as self-starting under load and smooth torque production. Compared with other expander concepts, the rotary vane expander has simpler structure, easier manufacturing and lower cost [98]. Advantages to the rotary vane expanders include flat operating efficiency curves over a wide range of conditions, low speeds (approximately 3000 rpm) that can match generator speeds without a gearbox, the ability to operate in the presence of liquids and wet vapors, minimal maintenance with little lubrication requirement, and proven operation with organic working fluids [99]. They also have several positive characteristics such as low noise- vibration and high volumetric expansion ratios as large as 10 [100]. They are also capable of handling high pressures [101].

In operation, the device must be lubricated to minimize wear and enhance sealing. A low number of contacting surfaces minimizes friction losses in these devices. Leakage has been found to be a larger contributor in performance loss than friction [101,102]. It needs to be pointed out that the rotational speed of a vane expander is strongly affected by the pressure and flow rate of the inlet compressed vapor. Further, due to the compressibility of the vapor and the mechanical friction, the RPM of the vane expander is actually nonlinear with its inlet pressure and it has hysteretic

Table 8
The comparison of various types of expanders suitable for ORC system.

Type	Capacity range (kW)	Rotate speed (rpm)	Cost	Advantages	Disadvantages
Radial-inflow turbine	50–500	8000–80,000	High	Light weight, mature manufacturability and high efficiency	High cost, low efficiency in off-design conditions and cannot bear two-phase
Scroll expander	1–10	<6000	Low	High efficiency, simple manufacture, light weight, low rotate speed and tolerable two-phase	Low Capacity, lubrication and modification requirement
Screw expander	15–200	<6000	Medium	Tolerable two-phase, low rotate speed and high efficiency in off-design conditions	Lubrication requirement, difficult manufacture and seal
Reciprocating piston expander	20–100	–	Medium	High pressure radio, mature manufacturability, adaptable in variable working condition and tolerable two-phase	Many movement parts, heavy weight, have valves and torque impulse
Rotary vane expander	1–10	<6000	Low	Tolerable two-phase, torque stable, simple structure, low cost and noise	Lubrication requirement and low capacity

behavior [82,103]. Another distinguishing feature of this type of rotary sliding vane expander is the injection of liberal quantity of lubricating oil directly into the expansion chamber, in order to seal each chamber from its neighbor and to lubricate the contact friction between the vanes and the stator as well [82].

Singh et al. [104] built and tested a prototype rotary vane expander in the laboratory. The experimental results were very close to the analytical values, and the performance efficiencies were recorded around 70% to 95% at the speed of rotation 2500–3000 rpm. The prototype experimental researches of rotary vane expanders are summarized in Table 7.

3.6. Various expanders' comparison and selection

There are many important parameters when selecting an expander such as high isentropic efficiency, pressure ratio, power output, lubrication requirements, complexity, rotational speed, dynamic balance, reliability and cost. Qiu et al. [82] mentioned that when selecting expanders, there are other factors than efficiency and cost that need to be considered, such as working temperatures and pressures, leaking, noise and safety. Table 7 shows the prototype researches of various types of expansion machines.

From the summary of the prototype researches, it can be seen that the study about radial-inflow turbine and scroll expander are in the majority. Regarding to working fluids, they are mainly R123, R134a, R245fa and CO_2. The highest isentropic efficiency could reach 85% using radial-inflow turbine, while the lowest value is about10%. Because most researches are conducted in the laboratory, the capacity are mainly less than 2 kW. The rotate speed of radial-inflow turbine is the largest within the range of 17,000–65,000 rpm, while the highest rotate speed for volume type expansion machines is 4800 rpm. The pressure ratio is generally within 5, which should be taken into consideration when designing a practical system.

The comparison of various types of expanders suitable for ORC system is shown in Table 8. From Table 8, it can be seen that according to the power capacity, radial-inflow turbine is maximum, which is suitable for the large capacity system. And for volume type expansion machines, screw and reciprocating piston expanders can also output relative high power, which can be applied to small and medium-sized system. The capacity of scroll and rotary vane expander is minimum, generally applied in small or micro ORC system.

In the aspect of rotate speed, single stage radial-inflow turbine's is rather high, which puts forward strict requirements on bearing, shaft seal and the strength of the rotating parts, resulting in higher design and manufacturing cost of speed type expansion machine. In comparison, the rotate speed of volume type expansion machine is low, usually less than 6000 rpm, and this kind of speed for bearing and shaft seal has low requirements, and more easy to implement.

From angle of the design and manufacturing cost, turbine design and manufacturing are highly difficult, and it's beneficial to be applied in large capacity. While the manufacturing and cost of various types of volume type expansion machine are relatively low, for example, vortex type expansion line of scroll expander is usually round involutes, which could be processed by four axle linkage-milling machines having *C* axis.

For the system operation, in some operating conditions (wet fluids with limited superheat at the expander supply), liquid may appear at the end of the expansion. This could be a threat of damage for radial-inflow turbine but not for scroll and screw expanders, since the latter can generally accept a large mass fraction of liquid. A major difficulty associated with the use of a positive displacement machine is its lubrication, which needs installing an oil separator and increases system complexity. Alternatively, oil-free machines can be used, but generally show lower volumetric performance and high leakage due to larger tolerances between moving parts.

4. The knowledge gaps and development directions

The common development process for a thermodynamic cycle system is shown in Fig. 7. First of all, the clear application background and working condition (cold/heat source temperature and energy load size, etc.), i.e. the basic conditions, are put forward; then, the basic thermodynamic cycle is constructed according to the basic conditions, and in combination with the specific nature of working fluids, the thermal process is clear and important state point is determine, thus completing the design cycle; thirdly, the study combining the actual performance of various thermal process with working fluids is carrying out, including the flow property and thermal performance, etc., and meanwhile, the researches on some mechanical devices such as expansion machines, are necessary; finally, with the application of the system, various auxiliary institutions will constantly improve, including control software and accessory parts etc.

From the review of the current literatures, most researches have focused on the second step and third step. The selection of working fluid is the key core of the whole thermodynamic cycle, and so in the future direction, how to screen an economic, environmental and efficient working fluid according to the different application background (i.e. solar energy, geothermal energy, waste heat energy, biomass energy, etc.) and different heat source temperature is also very important. For pure working fluids, the heat transfer characteristics, flammability and material compatibility of working fluids should be put into more effort while for mixed working fluids, the thermal physical properties and heat transfer characteristics of them are more urgent.

At the same time it can be found from the literatures, the experimental researches of ORC are very limited, especially for the organic expander research. Most of the researches are directly based on the built or renovated expansion machines, but expansion machine design research is lacked, and meanwhile, the aerodynamic characteristics of the working fluids are also needed.

From the view of working condition, the study on the evaporation temperature ranging from 200 °C to 350 °C is very limited. Due to the relatively low efficiency and simple system structure for the ORCs, how to effectively combine the ORC with other thermodynamic cycle forms is a development direction in the future. The off-design operating characteristics and control strategy for the ORCs are very necessary work in ORC application process.

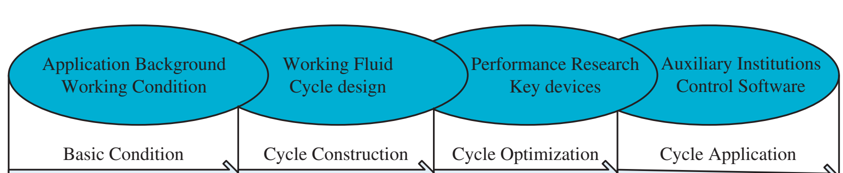

Fig. 7. The development process of a thermodynamic cycle.

5. Conclusion

This paper presents a comprehensive review of working fluid selection (including pure fluids and mixtures) and the choice of expansion machines working in the ORC system. The types of working fluids (mainly dry or wet) will affect the operation and layout of the system; the thermal physical properties of working fluids can be used as a performance index for comparison between different fluids, and of which, the ratio of vaporization latent heat and sensible heat, critical parameters and molecular complexity are more important; the selection of working fluid is a tedious process, influenced by heat source types, temperature level and the performance indexes, which should be included in the every design process of ORC plants; mixed working fluids have good temperature matching to improve the overall efficiency, but the screening of mixture compositions and fractions need further been researched; the process of working fluid selection is limited to the operating conditions, working fluid characteristics, equipment structures and environmental safety considerations, and these limitations can be used in the preselection and recleaning of working fluids; the selection of expansion machines should consider many factors, such as the power capacity, isentropic efficiency, cost and complexity etc., and different expansion machines have their own applicable scope so that reasonable selection is based on system operation and working conditions.

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